VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME .....

CT GROUP .....

CHEMISTRY 9729/03

Paper 3 Free Response **19 September 2023**

Candidates answer on the Question Paper. **2 hours**
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and CT group in the spaces at the top of this page.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
Section A	1	/ 24
	2	/ 16
	3	/ 20
Section B	4	/ 20
	OR 5	/ 20
Total		/ 80

This document consists of **28** printed pages.

Section A

Answer **all** the questions in this section.

1 **(a)** Describe and explain the trend in thermal stability of the hydrogen halides. [2]

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(b) A sodium salt of the interhalogen ion, IBr_x^- is prepared. When heated, the salt evolves bromine vapour, leaving sodium iodide as the residue.

The bromine vapour evolved requires 32.0 cm^3 of 0.100 mol dm^{-3} of aqueous sodium thiosulfate for complete reaction. The balanced ionic equation for the reaction between bromine and thiosulfate is as shown below.

$$S_2O_3^{2-}(aq) + 4Br_2(g) + 5H_2O(l) \rightarrow 2SO_4^{2-}(aq) + 8Br^-(aq) + 10H^+(aq)$$

(i) Construct a balanced equation for the thermal decomposition of $NaIBr_x$. [1]

(ii) Calculate the amount of bromine gas evolved. [1]

The sodium iodide residue was completely reacted with concentrated sulfuric acid to give HI gas, which immediately further reacted with concentrated sulfuric acid to give H_2S, together with black crystals of iodine. The mass of the iodine crystals formed was found to be 1.63 g.

(iii) Calculate the amount of iodine formed and hence deduce the formula of the interhalogen ion. [2]

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(c) Chloroalkanes and bromoalkanes can be made by the reaction of the corresponding halogen with alkanes. One example is given below.

$$CH_3CH_2CH_3 + Cl_2 \rightarrow CH_3CH_2CH_2Cl + HCl$$

(i) State the conditions needed for this reaction. [1]

(ii) Name and describe the mechanism of this reaction. [2]

(iii) Suggest why it is **not** possible to make iodoalkanes by this method. [1]

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(d) Suggest a structural formula for each of the compounds, **A** to **D**, in the following schemes shown in Figure 1.1. [4]

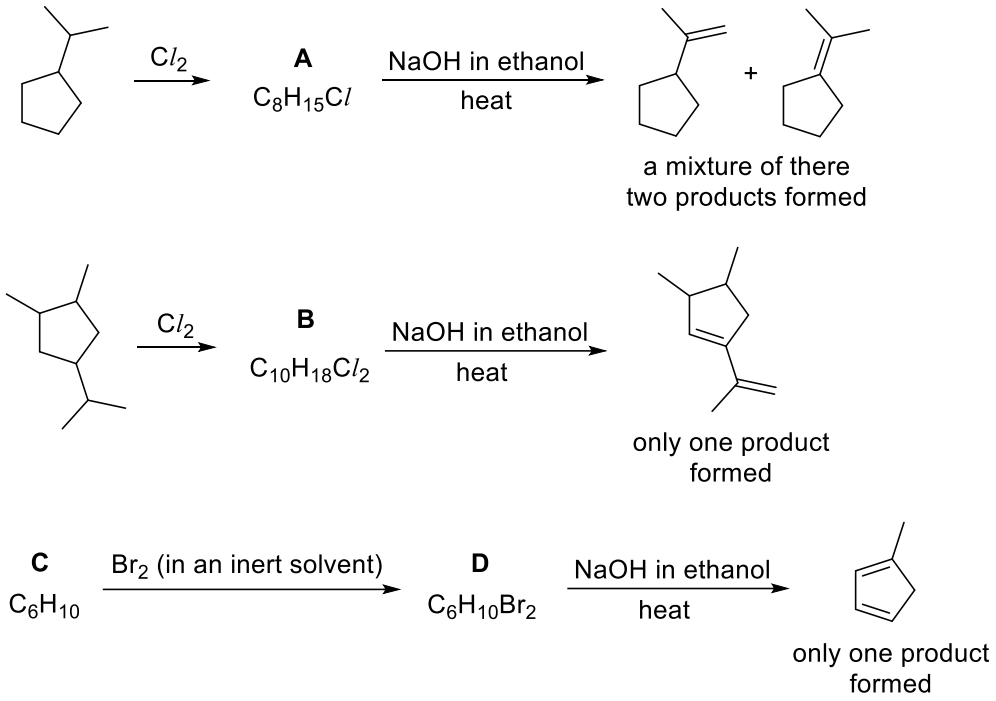

Figure 1.1

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(e) Chlorofluoroalkanes, CFCs, were once used as refrigerant fluids and aerosol propellants. In many applications they have now been replaced by alkanes. This is because CFCs contribute to the destruction of the ozone layer.

(i) Suggest one reason why CFCs were originally used for these purposes. [1]

(ii) Explain how CFCs destroy the ozone layer. [1]

(iii) Suggest one potential hazard of using alkanes instead of CFCs. [1]

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(f) Figure 1.2 shows two reactions involving benzene and a suitable Lewis acid as a catalyst.

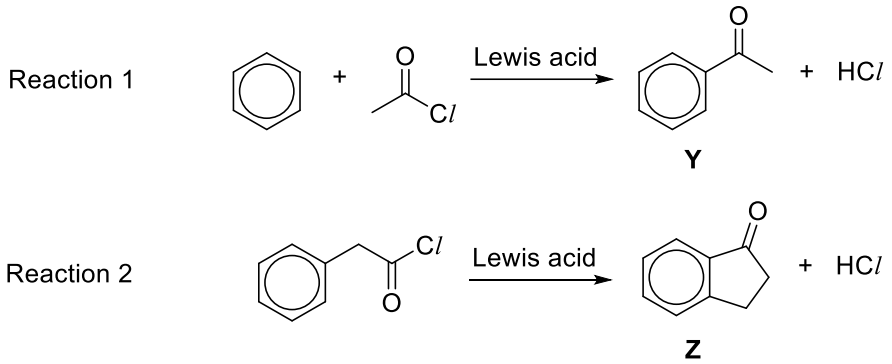

Figure 1.2

(i) Suggest the type of reaction for reaction 1. [1]

(ii) Suggest the reagents and conditions for a reaction that could be used to distinguish between **Y** and **Z**, and describe the observations. [2]

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(g) When benzene is added to compound **Q** in the presence of A*l*C*l*$_3$, Compound **E** with the molecular formula of $C_{10}H_{12}$ is formed.

When **E** is heated with acidified $KMnO_4$, **F** is formed and effervescence is also observed,

F contains 57.8% of carbon, 3.6% of hydrogen and 38.6% of oxygen by mass. The relative molecular mass of **F** is 166. 1 mol of **F** readily reacts with 2 mol of NaOH(aq).

(i) Determine the molecular formula of **F** [1]

(ii) Hence, suggest the structure for **Q**, **E** and **F**. [3]

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2 **(a)** Describe what is meant by the term *nucleon number*. [1]

(b) State two ways in which the behaviour of electrons in an electric field differs from that of protons. [1]

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(c) A mixture of $HC_2O_4^-$ and $C_2O_4^{2-}$ can act as a buffer in biochemical and molecular biology experiments.

(i) Write an expression for K_b of $C_2O_4^{2-}$, stating its units. [1]

(ii) The pK_b value of $C_2O_4^{2-}$ is 9.72.

Determine the amount of hydrochloric acid is needed to add to a 1.00 dm^3 solution of 0.0100 mol dm^{-3} $K_2C_2O_4$ solution so that a buffer solution with a pH of 5.0 can be prepared.

You may assume that the volume of solution remains the same with the addition of hydrochloric acid. [2]

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At 298 K, the K_{sp} of silver(I) ethanedioate, $Ag_2C_2O_4$ is 5.40×10^{-12} mol^3 dm^{-9}.

(iii) Determine whether precipitation will be observed when 0.500 mg of $AgNO_3$ solid was added to 25.0 cm^3 of 3.50×10^{-3} mol dm^{-3} $Na_2C_2O_4$. [You can ignore hydrolysis of $C_2O_4^{2-}$ in your calculation] [2]

(iv) Explain why the solubility of $Ag_2C_2O_4$ increases when aqueous NH_3 is added. [2]

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(d) The initial rate of the reaction between persulfate and iodide ions can be studied by the clock method, using sodium thiosulfate. The equations for the reactions are as follows.

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2 \qquad \text{reaction 1}$$

$$2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-} \qquad \text{reaction 2}$$

The reaction between $S_2O_8^{2-}$ and I^- ions is very slow. If a small amount of aqueous iron(II) ions is added to the mixture, the rate of reaction increases.

(i) By using the concept of activation energy and an appropriate sketch of the Boltzmann distribution, explain why the addition of iron(II) ions speeds up the reaction. [3]

(ii) Write equations to show how iron(II) ions is used as catalyst. [2]

(iii) Sketch an energy profile diagram for the catalysed reaction. Label the activation energies, enthalpy change of reaction, and identity of the species present as reactants, intermediates and products clearly on the diagram. [2]

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[Total: 16]

3 (a) (i) Iodine and chlorine react together to form iodine monochloride.

$$I_2(s) + Cl_2(g) \rightarrow 2ICl(s)$$

Explain the term, *bond energy*, with reference to I-C*l* bond. [1]

(ii) Construct a fully labelled energy cycle to calculate the bond energy of the I–C*l* bond in IC*l*.

Your cycle should include relevant data from the *Data Booklet* together with the following data:

standard enthalpy change of formation, ($\Delta H_f^{\ominus}$) of IC*l*(s) = –35.5 kJ mol^{-1}
enthalpy change of sublimation of $I_2(s) \rightarrow I_2(g)$ = +62.4 kJ mol^{-1}
enthalpy change of sublimation of $ICl(s) \rightarrow ICl(g)$ = +52.9 kJ mol^{-1} [3]

(iii) The standard Gibbs free energy of formation, $\Delta G_f^{\ominus}$, of IC*l*(s) is +7.19 kJ mol^{-1}.

Calculate $\Delta S_f^{\ominus}$ and comment on its sign with respect to the reaction. [2]

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(b) Figure 3.1 shows a synthesis scheme involving iodine monochloride in one of the steps.

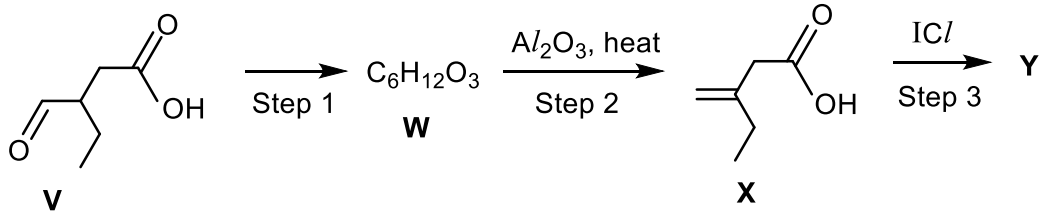

Figure 3.1

(i) Draw the structure of **W** and state the reagents and conditions for Step 1. [2]

(ii) **Y** is the major product of the reaction in Step 3.
Suggest the structure of **Y**. [1]

(iii) When I_2 is used as the reagent instead of ICl in Step 3, the reaction occurs less readily. Suggest an explanation for this observation. [1]

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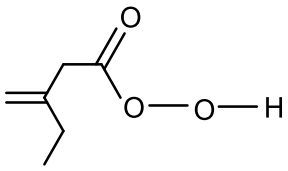
(c) Peroxyacids are compounds containing the $–CO_3H$ group. The structure of **Z**, which contains the $–CO_3H$ group, is shown below.



Z

Suggest why **Z** has a higher pK_a value than **X**. [2]

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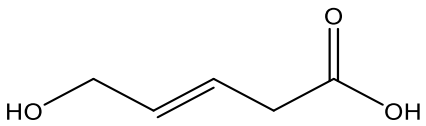
(d) **B** and **C** are isomers with the molecular formula $C_5H_6O_2$.

B forms a brick-red precipitate with Fehling's solution but does not give effervescence with sodium.

C reacts with hot aqueous sodium hydroxide. Upon acidification, it forms the product shown below.



When **B** and **C** are separately reacted with hot acidified $KMnO_4$, they form the same mixture of organic products, **D** ($C_3H_4O_4$) and **E** ($C_2H_2O_4$). **E** undergoes further oxidation to give effervescence.

Deduce the structures of **B** to **E**, and explain the chemistry involved. [8]

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Section B

Answer **one** question from this section.

4 (a) Chromium is the Earth's 21st most abundant element and the 6th most abundant transition metal. The most common oxidation state of chromium is +3.

(i) Write an equation, with state symbols, to show a possible way of converting chromium metal to a compound with chromium in its +3 oxidation state. [1]

(ii) Hydrated chromium(III) chloride exists as isomers, with the general formula of $CrCl_3 \cdot 6H_2O$. Each of the isomers is of a different colour. One such isomer is the hydrated dark green compound $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$.

Give the formula of two other isomers of hydrated chromium(III) chloride with a coordination number of 6. [1]

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Figure 4.1 shows some reactions of chromium(III) chloride.

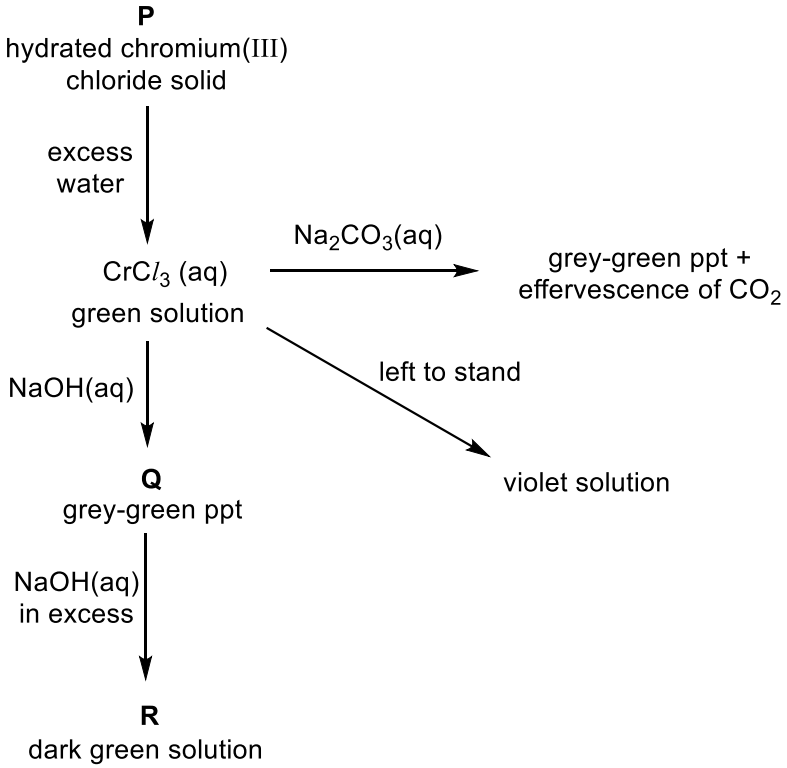

Figure 4.1

(iii) Explain why carbon dioxide is evolved when $Na_2CO_3(aq)$ is added to aqueous chromium(III) chloride. Include any relevant equations in your answer. [1]

(iv) Identify the grey-green precipitate **Q**. [1]

(v) Suggest a formula for the complex ion present in **R**. [1]

(vi) A student conducted an experiment where he reacted zinc metal with a solution of acidified dichromate(VI) ions. He observed several changes in colour: the orange solution first turned green then bright blue.

Use $E^{\ominus}$ values from the *Data Booklet* to explain all the colour changes that are taking place. Write equations for the reactions that occurred. [3]

(vii) Explain why a solution of chromium(III) chloride is coloured. [2]

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(b) The oxides of phosphorus and sulfur react with water.

Write equations for reaction between oxides of phosphorus and sulfur with water. Describe the effect of the resulting solutions on Universal Indicator solution. [3]

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(c) Sulfuric acid is manufactured in a series of steps, starting with sulfur. In one of these steps, sulfur dioxide is oxidised in a reversible reaction.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

(i) The initial partial pressures of $SO_2(g)$ and $O_2(g)$ are 100 kPa and 50 kPa respectively at a fixed temperature in a closed vessel having a fixed volume. Given that the total pressure at equilibrium is 110 kPa, calculate K_p for this equilibrium. Include the units of K_p in your answer. [2]

(ii) The above reaction is catalysed by vanadium(V) oxide, V_2O_5. Explain the mode of action of V_2O_5 in the reaction. [2]

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(d) Copper(II) oxide is produced on a large scale in the process of extracting copper from its ores.

When concentrated hydrochloric acid is added to solid copper(II) oxide, the black CuO dissolves to form a dark yellow solution. When water is subsequently added in excess, a blue solution is formed.

Suggest an explanation for the observations described. Include relevant equations in your answer. [3]

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5 *Use of the Data Booklet is relevant for this question.*

This question explores the chemistry of various transition elements.

(a) The stability constant of a transition metal complex, K_{stab}, is an equilibrium constant associated with the following reaction.

$$M(H_2O)_6^{n+}(aq) + mL(aq) \rightleftharpoons ML_m(H_2O)_{6-m}^{n+}(aq) + mH_2O(l) \quad \text{where L is a ligand.}$$

For example, the stability constant of the complex formed when excess NH_3 is added to $Cu^{2+}(aq)$ is as shown:

$$K_{stab} = \frac{[[Cu(NH_3)_4(H_2O)_2]^{2+}]}{[[Cu(H_2O)_6]^{2+}][NH_3]^4}$$

(i) Explain what is meant by the term *transition element*. [1]

The following table lists some iron complexes together with their colours and their stability constants.

complex	colour	K_{stab}
$[Fe(SCN)(H_2O)_5]^{2+}(aq)$	deep red	1×10^2
$[FeF_6]^{3-}(aq)$	colourless	2×10^{15}
$[Fe(CN)_6]^{4-}(aq)$	pale yellow	1×10^{24}
$[Fe(CN)_6]^{3-}(aq)$	orange-yellow	1×10^{31}
$[Fe(H_2O)_6]^{3+}(aq)$	yellow	-

(ii) Use the data in the table to predict and explain what will be observed when a solution of $Fe^{3+}(aq)$ is treated with excess KSCN(aq). Include relevant equation(s) where appropriate. [1]

(iii) As shown by their $E^{\ominus}$ values, $Fe(CN)_6^{3-}(aq)$ is a weaker oxidising agent than $Fe^{3+}(aq)$. Use the data in the table above to explain why this is the case. [2]

(iv) $FeF_6^{3-}(aq)$ is unusual in that it is colourless despite the occurrence of d-d transition just as in typical Fe(III) species. Suggest a reason for this observation. [1]

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(b) **(i)** Describe the electrolytic purification of copper, which contains the impurities silver and nickel. In your answer you should discuss about the nature of the electrodes, the electrolyte used and the reactions occurring at the anode and cathode with reference to relevant $E^{\ominus}$ values from the *Data Booklet*. [3]

Adding KI(aq) to a solution containing $Cu^{2+}(aq)$ causes a reaction to take place, which produces brown solution and a white precipitate. Upon adding $Na_2S_2O_3$, the brown solution turns colourless.

(ii) Construct a balanced equation for the reaction between $Cu^{2+}(aq)$ and $I^{-}(aq)$. [1]

(iii) By selecting appropriate $E^{\ominus}$ values from the *Data Booklet,* explain why it would be expected that this redox reaction would not occur. [2]

(iv) Suggest a possible reason for why it does in fact occur. [1]

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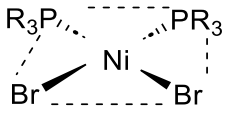
(c) Molecules **D** and **E** with the structural formula $NiBr_2(PR_3)_2$ (where R = phenyl) are *cis-trans* isomers. The molecules differ in the spatial arrangements of the ligands around the central metal ion.

Both isomers are planar and the ligand-metal-ligand bond angle in the plane of the molecule is 90°. The structure of molecule **D**, the *cis* isomer is shown in Figure 5.1.



Molecule **D**

Figure 5.1

(i) State the coordination number of Ni in molecule **D**. [1]

(ii) Draw the 3-dimensional structure of molecule **E** which exist in the *trans* isomer. [1]

(iii) Molecule **F**, is another isomer of **D**. It has a dipole moment just like **D**. The coordination number of Ni in molecule **F** is the same as that in **D**.

Suggest and draw a possible structure of **F**. [1]

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(d) A hot solution of sodium tartrate reacts with hydrogen peroxide giving a very slow stream of carbon dioxide.

When a few drops of an aqueous cobalt(II) salt is added to the mixture, a pink colour is seen. Soon the colour of the solution turns green and a vigorous effervescence of carbon dioxide takes place. When the reaction stops the pink colour is restored.

(i) What is the role of the cobalt(II) salt in the reaction? [1]

(ii) With reference to the observations above, give reasons which support your answer in **(d)(i)**. [2]

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(e) $CoCO_3$ decomposes at approximately 295°C whereas $CuCO_3$ decomposes at approximately 335°C.

By quoting relevant data from the *Data Booklet*, explain the difference in decomposition temperature of these two compounds. [2]

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Additional answer space

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